The momentum distribution of a one-dimensional ideal gas of N atoms

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We calculate the average momentum distribution and the average deviation from this distribution for a one-dimensional ideal gas of N atoms. The calculation is performed using analytical and numerical methods, and the results obtained using the two methods are compared. We use these results to show that in the limit of large N, almost all the possible microstates of an ideal gas have momentum distributions that are very close to the Maxwell distribution. We discuss the significance of this fact for understanding why an ideal gas approaches thermal equilibrium.

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I. INTRODUCTION

Consider a classical ideal gas of N atoms in thermal equilibrium. In the limit of infinite N the average momentum distribution of the gas is the Maxwell distribution, and the average deviation from this distribution is zero. In this paper we calculate the average momentum distribution and average deviation for finite values of N. Our results hold even for an ideal gas of just a few atoms and provide a simple example of thermodynamics in the context of a few-body system. Few-body systems play an important role in fields of current interest, such as nanotechnology and biophysics, and there is an increasing need to understand the thermodynamics of such systems.

We calculate the average momentum distribution and average deviation using two methods. First, we perform the calculation via a simple numerical experiment that relies on a minimum of mathematics and can be understood by students with little prior background in statistical mechanics.[1] We also perform the calculation analytically. Instructors can present either the numerical calculation or the analytic calculation depending on the level of the students.

We use our results to establish an important property of the Maxwell distribution. The Maxwell distribution has two properties that help explain the thermodynamic behavior of an ideal gas. First, for an ideal gas of fixed volume V, atom number N, and total energy E, the Maxwell distribution is the unique distribution that maximizes the entropy. Second, for large N almost all the possible microstates of such a gas have momentum distributions that are very close to the Maxwell distribution. The first property tells us that the entropy is maximized when the gas is in thermal equilibrium. The second property tells us that if the gas is not in thermal equilibrium, then it will tend to approach thermal equilibrium because there are vastly more microstates that have Maxwellian distributions than microstates that have non-Maxwellian distributions.[2]

Although both properties are important, only the first property is usually discussed in most elementary textbooks.[3,4] We use our results to give a proof of the second property of the Maxwell distribution that is simpler than existing proofs and offers greater physical insight.[5]

II. THE IDEAL GAS

Consider a one-dimensional ideal gas of N identical atoms of mass m. We let x_n and p_n denote the position and momentum of atom number n and define vectors $\vec{x}=(x_1,\ldots,x_N)$ and $\vec{p}=(p_1,\ldots,p_N)$. These vectors serve as canonical coordinates for the $2N$-dimensional phase space of the system. We assume that the atoms are confined to a region of fixed length L, so $0\le x_n\le L$. Also, we assume that the total energy E of the system is conserved, so $\vec{p}\cdot\vec{p}/2m=E$. This relation tells us that the vector $\vec{p}$ must lie on an N-sphere[6] of radius $\sqrt{N}\bar{p}$, where $\bar{p}\equiv(2mE/N)^{1/2}$ is the root-mean-squared momentum of the atoms. The points in phase space that satisfy these conditions define a $(2N-1)$-dimensional subspace of possible microstates. We call this subspace the state space of the system.

Given a microstate $\{\vec{x},\vec{p}\}$, we define a function $P(p)$ that gives the fraction of atoms that have momenta within $\delta p/2$ of p. We can express this function as

$$P(p)=\frac{1}{N}\sum_{n=1}^{N}\Theta_n(p), \tag{1}$$

where $\Theta_n(p)\equiv\theta(\delta p/2-|p-p_n|)$ is one if atom number n is within $\delta p/2$ of p and zero otherwise.[7] For small values of δp the momentum distribution of the atoms is given by $f(p)\simeq(1/\delta p)P(p)$. Our goal is to show that for large N, almost all the microstates in state space have distributions $f(p)$ that are very close to the Maxwell distribution $f_M(p)$, which is given by

$$f_M(p)=(2\pi\bar{p}^2)^{-1/2}e^{-p^2/2\bar{p}^2}. \tag{2}$$

We will establish this result by averaging various quantities over the state space of the gas. The averaging can be performed by appealing to Liouville's theorem and the ergodic hypothesis. Liouville's theorem says that state space volumes are preserved under time evolution, and the ergodic hypothesis says that if we evolve the system over sufficiently long times, it will come arbitrarily close to every point in state space. Together, these results give a probability measure on state space: the probability that the system occupies a given region of state space is proportional to the volume of the region.

By using this probability measure, we can average $P(p)$ over all the microstates in state space. We denote this average by $\langle P(p)\rangle$ and define the quantity

$$D(p)=(P(p)-\langle P(p)\rangle)^2 \tag{3}$$

as a measure of the deviation of $P(p)$ from its average value $\langle P(p)\rangle$. We can also average $D(p)$ over the entire state space;

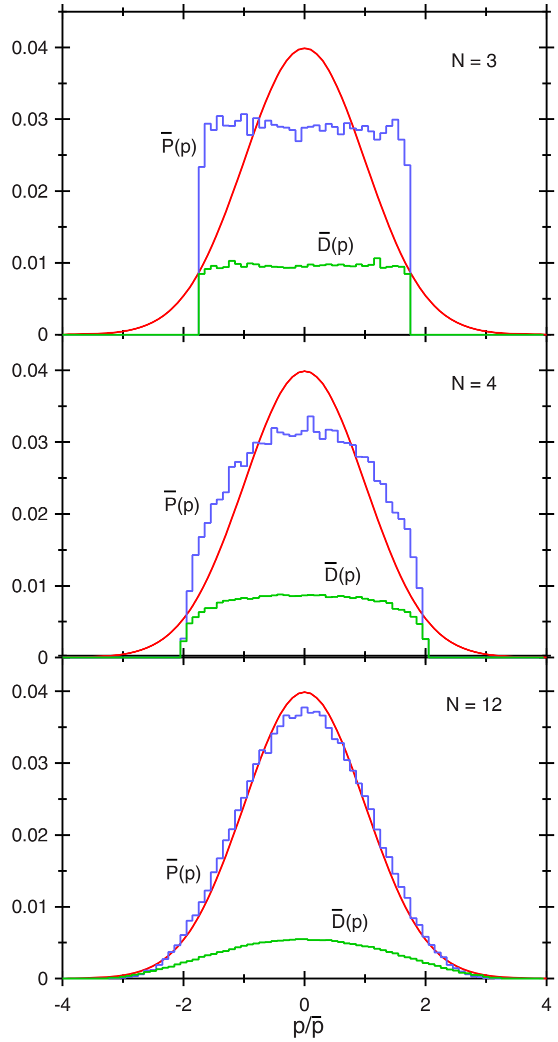

Fig. 1. The distributions $\bar{P}(p)$ and $\bar{D}(p)$ versus $p/\bar{p}$ for $N=3$, 4, and 12 (jagged curves). The smooth curves are $P_M(p)$. For these graphs $\delta p/\bar{p}=0.1$ and $K=10^4$.

we denote this average by $\langle D(p)\rangle$. Our desired result amounts to two claims. First, we claim that for $\delta p \ll \bar{p}$ and $N\to\infty$,

$$\langle P(p)\rangle \to P_M(p), \tag{4}$$

where $P_M(p)\equiv f_M(p)\delta p$. Second, we claim that for $\delta p \ll \bar{p}$ and $N\geq 2$,

$$\langle D(p)\rangle \simeq (1/N)\langle P(p)\rangle. \tag{5}$$

Equation (4) asserts that for large N, the average distribution approaches the Maxwell distribution, and Eq. (5) asserts that the deviation from the average scales like $1/N$, and hence vanishes in the limit $N\to\infty$.[8]

In Sec. IV we will derive Eqs. (4) and (5) by integrating $P(p)$ and $D(p)$ over the entire state space, but first we describe a simpler way of motivating these equations that relies on a numerical estimation of $\langle P(p)\rangle$ and $\langle D(p)\rangle$.

III. NUMERICAL EXPERIMENT

We can numerically compute $\langle P(p)\rangle$ and $\langle D(p)\rangle$ using the following procedure. First, we randomly choose K microstates from state space. For each microstate we compute $P(p)$ using Eq. (1); let $P_k(p)$ denote the result of this computation for microstate k. We define

$$\bar{P}(p) = \frac{1}{K}\sum_{k=1}^{K} P_k(p), \tag{6}$$

$$\bar{D}(p) = \frac{1}{K}\sum_{k=1}^{K} [P_k(p) - \bar{P}(p)]^2. \tag{7}$$

For large values of K we expect that $\bar{P}(p)\simeq\langle P(p)\rangle$ and $\bar{D}(p)\simeq\langle D(p)\rangle$.

It is important that we choose the microstates using the probability measure provided by Liouville's theorem and the ergodic hypothesis. Thus, to randomly choose a microstate $\{\vec{x},\vec{p}\}$, we must choose $\vec{p}$ with uniform probability over the surface of a N-sphere of radius $\sqrt{N}\bar{p}$. Because $\vec{x}$ is not used in computing $\bar{P}(p)$ or $\bar{D}(p)$, we do not bother to choose it.

We choose $\vec{p}$ using the following algorithm. Assume that we have a random number generator that produces numbers uniformly distributed from 0 to 1. We use the generator to choose N random numbers $r_1,\ldots,r_N$, and we define a vector $\vec{r}=(2r_1-1,\ldots,2r_N-1)$. If $|\vec{r}|>1$, we throw out this vector and generate a new vector; we keep trying until we obtain a vector whose magnitude is less than 1.[9] This algorithm produces vectors $\hat{r}=\vec{r}/|\vec{r}|$ that are uniformly distributed over the unit N-sphere. We use this algorithm to determine $\hat{r}$ and then define $\vec{p}=\sqrt{N}\bar{p}\hat{r}$ to randomly choose $\vec{p}$.

In Fig. 1 we use this algorithm to estimate $\bar{P}(p)$ and $\bar{D}(p)$ for several values of N.[10] We find that as N increases $\bar{P}(p)$ approaches $P_M(p)$, as stated in Eq. (4). We also see that as N increases $\bar{D}(p)$ decreases.

In Fig. 2 we quantify the decrease in $\bar{D}(p)$ by plotting $\bar{P}(0)/\bar{D}(0)$ as a function of N. We find that the numerical calculation agrees well with the result $\bar{P}(0)/\bar{D}(0)\simeq N$ stated in Eq. (5).

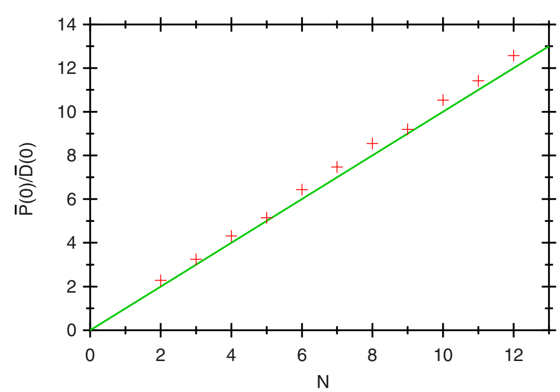

Fig. 2. $\bar{P}(0)/\bar{D}(0)$ versus N. The points are from the numerical experiment, and the solid line is $\bar{P}(0)/\bar{D}(0)=N$; $\delta p/\bar{p}$ and K are the same as in Fig. 1.

IV. EXACT CALCULATION

We now derive Eqs. (4) and (5) by integrating $P(p)$ and $D(p)$ over the entire state space. In what follows we will assume that $N \geq 3$.

Given a quantity $A = A[\vec{p}]$ that depends on the momentum state of the gas, we can express the average of A over all the microstates in the state space as

$$\langle A \rangle = \frac{1}{V}\left(\prod_{n=1}^{N} \int dp_n\right) A[\vec{p}]\,\delta(E - \vec{p}\cdot\vec{p}/2m), \tag{8}$$

where

$$V = \left(\prod_{n=1}^{N} \int dp_n\right) \delta(E - \vec{p}\cdot\vec{p}/2m). \tag{9}$$

We can calculate V by defining $R = |\vec{p}|$ and working in spherical coordinates:

$$V = \Omega_N \int_0^{\infty} \delta(E - R^2/2m) R^{N-1} dR \tag{10a}$$

$$= m\Omega_N (2mE)^{(N-2)/2}, \tag{10b}$$

where Ω_N, the total solid angle for the unit N-sphere, is given by[11]

$$\Omega_N = 2\pi^{N/2}/\Gamma(N/2). \tag{11}$$

We use Eq. (8) to calculate $\langle P(p)\rangle$. By symmetry $\langle \Theta_n(p)\rangle = \langle \Theta_N(p)\rangle$, so

$$\langle P(p)\rangle = \frac{1}{N}\sum_{n=1}^{N} \langle \Theta_n(p)\rangle = \langle \Theta_N(p)\rangle. \tag{12}$$

For $\delta p \ll \bar{p}$ we can approximate $\Theta_N(p)$ by a delta function:

$$\langle P(p)\rangle = \langle \Theta_N(p)\rangle \simeq \delta p \langle \delta(p - p_N)\rangle. \tag{13}$$

We now use Eq. (8) to calculate the average. We can perform the integrals by defining $R = (p_1^2 + \ldots + p_{N-1}^2)^{1/2}$ and working in spherical coordinates:

$$\left(\prod_{n=1}^{N} \int dp_n\right) \delta(p - p_N)\,\delta(E - \vec{p}\cdot\vec{p}/2m)$$

$$= \Omega_{N-1} \int_0^{\infty} \delta(E - (R^2 + p^2)/2m) R^{N-2} dR \tag{14a}$$

$$= m\Omega_{N-1}(2mE - p^2)^{(N-3)/2}. \tag{14b}$$

We collect Eqs. (8), (10), (13), and (14) and find that[12,13]

$$\langle P(p)\rangle = \langle \Theta_N(p)\rangle = \frac{1}{\sqrt{N}}\frac{\Omega_{N-1}}{\Omega_N}(\delta p/\bar{p})(1 - p^2/N\bar{p}^2)^{(N-3)/2}. \tag{15}$$

Equation (15) gives us an exact expression for $\langle P(p)\rangle$ for finite values of N. In Fig. 3 we compare this exact expression with the numerical experiment for $N=4$ and find good agreement.

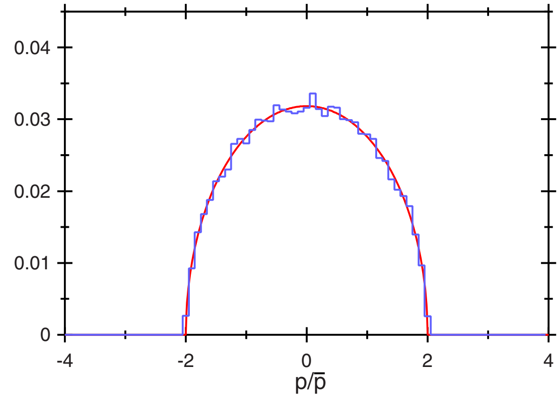

Fig. 3. $\langle P(p)\rangle$ versus $p/\bar{p}$ for $N=4$. The jagged curve is from the numerical experiment and duplicates the curve shown in Fig. 1; the smooth curve is the exact result given by Eq. (15).

We can verify Eq. (4) by taking the $N \to \infty$ limit of Eq. (15). Note that $(1 - p^2/N\bar{p}^2)^{(N-3)/2} \to \exp(-p^2/2\bar{p}^2)$. From Eq. (11) we find that $\Omega_{N-1}/\Omega_N \to (N/2\pi)^{1/2}$. Thus, $\langle P(p)\rangle \to P_M(p)$, as stated in Eq. (4).

We next use Eq. (8) to calculate $\langle D(p)\rangle$. We substitute Eq. (1) into Eq. (3) and find that

$$\langle D(p)\rangle = (1/N)\langle \Theta_N(p)\rangle + (1 - 1/N)\langle \Theta_N(p)\Theta_{N-1}(p)\rangle - \langle \Theta_N(p)\rangle^2. \tag{16}$$

We have used the fact that $\langle \Theta_n^2(p)\rangle = \langle \Theta_n(p)\rangle$, and that by symmetry $\langle \Theta_n(p)\rangle = \langle \Theta_N(p)\rangle$ and $\langle \Theta_i(p)\Theta_j(p)\rangle = \langle \Theta_N(p)\Theta_{N-1}(p)\rangle$ for $i \neq j$. We calculate $\langle \Theta_N(p)\Theta_{N-1}(p)\rangle$ using the same methods we used to calculate $\langle P(p)\rangle$ and find that

$$\langle \Theta_N(p)\Theta_{N-1}(p)\rangle = \frac{1}{N}\frac{\Omega_{N-2}}{\Omega_N}(\delta p/\bar{p})^2(1 - 2p^2/N\bar{p}^2)^{(N-4)/2}. \tag{17}$$

Let us now consider two limits of Eq. (16).

First consider the limit $N \ll \bar{p}/\delta p$. One can show that for $N \geq 3$, the factors $N^{-1/2}(\Omega_{N-1}/\Omega_N)$ and $N^{-1}(\Omega_{N-2}/\Omega_N)$ are of order unity. Thus, from Eqs. (15) and (17), it follows that the first term of Eq. (16) is of order $(1/N)(\delta p/\bar{p})$ and the second and third terms are of order $(\delta p/\bar{p})^2$. Thus, the first term dominates, and we obtain Eq. (5).

Now consider the limit $N \gg 1$. We can express Eq. (16) as

$$\langle D(p)\rangle = (1/N)\langle \Theta_N(p)\rangle + C(p) - (1/N)\langle \Theta_N(p)\Theta_{N-1}(p)\rangle, \tag{18}$$

where

$$C(p) \equiv \langle \Theta_N(p)\Theta_{N-1}(p)\rangle - \langle \Theta_N(p)\rangle\langle \Theta_{N-1}(p)\rangle \tag{19}$$

describes the correlation between the momentum values of pairs of atoms. We substitute Eqs. (15) and (17) into Eq. (19) and find that

$$C(p) \to -(1/4\pi)(1/N)(\delta p/\bar{p})^2(1 - p^2/\bar{p}^2)^2 e^{-p^2/\bar{p}^2} \tag{20}$$

in the limit $N \to \infty$. Equation (20) expresses the physically reasonable property that as $N \to \infty$, the momentum values of pairs of atoms become uncorrelated. From Eqs. (15), (17), and (20), it follows that the first term of Eq. (18) is of order

$(1/N)(\delta p/\bar{p})$ and the second and third terms are of order $(1/N)(\delta p/\bar{p})^2$. Thus, the first term dominates and again we obtain Eq. (5). Physically, this result follows from the fact that the momenta of the atoms are uncorrelated in the limit $N \to \infty$, and thus the probability $P_n(p)$ that there are n atoms within $\delta p/2$ of p is given by the Poisson distribution

$$P_n(p) = (1/n!)\bar{n}^n(p)e^{-\bar{n}(p)}, \tag{21}$$

where $\bar{n}(p) \equiv N\langle P(p)\rangle$ is the average number of atoms within $\delta p/2$ of p.

Because we are assuming that $\delta p/\bar{p} \ll 1$, either the limit $N \ll \bar{p}/\delta p$ or the limit $N \gg 1$ applies, and thus Eq. (5) is always valid for $N \geq 3$.[14]

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[1]The program used to perform the numerical experiment will be provided upon request.

[2]Computer simulations of the evolution of an ideal gas toward thermal equilibrium are discussed in J. Novak and A. B. Bortz, "The evolution of the two-dimensional Maxwell–Boltzmann distribution," Am. J. Phys. **38**(12), 1402–1406 (1970) and A. D. Boozer, "Time asymmetry in a dynamical model of the one-dimensional ideal gas," *ibid.* **76**(11), 1026–1030 (2008).

[3]The first property is established in K. Huang, *Statistical Mechanics*, 2nd ed. (Wiley, New York, 1987), Sec. 4.3.

[4]A close analog to the second property is sometimes established by employing the canonical rather than microcanonical ensemble. See, for example, R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford U. P., Oxford, 1938), p. 506.

[5]An overview of various proofs of this result is given in P. A. Mello and T. A. Brody, "A different proof of the Maxwell–Boltzmann distribution," Am. J. Phys. **40**(9), 1239–1245 (1972).

[6]By an "N-sphere" we mean a sphere in N-dimensional Euclidean space. According to this convention a circle is a 2-sphere.

[7]Here $\theta(x)$ is the step function, defined such that $\theta(x)=1$ for $x>1$, $\theta(x)=1/2$ for $x=0$, and $\theta(x)=0$ for $x<0$.

[8]Most treatments prove the equivalent of Eq. (5) only in the limit $N\to\infty$. As shown in Sec. IV, it holds for arbitrary N.

[9]One can show that the expected number of trials is $n(N)=2^N N/\Omega_N$, where Ω_N, the solid angle for the unit N-sphere, is given by Eq. (11). The function $n(N)$ grows very rapidly with increasing N, so this algorithm is practical only for small values of N.

[10]For simplicity we compute $\bar{P}(p)$ and $\bar{D}(p)$ only for values of p that are integer multiples of δp. This procedure is equivalent to making a histogram of the atom momenta in which the size of the momentum bins is δp.

[11]Equation (11) is derived in M. E. Peskin and D. V. Schroeder, *An Introduction to Quantum Field Theory* (Addison-Wesley, Reading, MA, 1995), p. 249.

[12]Equation (15) is derived in R. López-Ruiz and X. Calbert, "Derivation of the Maxwell distribution from the microcanonical ensemble," Am. J. Phys. **75**(8), 752–753 (2007), and in J. R. Ray and H. W. Graben, "Small systems have non-Maxwellian momentum distributions in the microcanonical ensemble," Phys. Rev. A **44**(10), 6905–6908 (1991).

[13]The analog to Eq. (15) for a two-dimensional ideal gas is derived in S. Velasco, J. A. White, and J. Guemez, "Single particle energy and velocity distributions for finite simple systems in the microcanonical ensemble," Eur. J. Phys. **14**(4), 166–170 (1993).

[14]One can show that Eq. (5) is also valid for $N=2$. This result must be established as a special case because Eq. (17) is not valid when $N=2$.